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(54) **Ink-receiving layers for ink-jet recording elements**

(57) An ink-jet recording element is provided comprising a polymeric film substrate or a resin coated paper substrate and coated thereon an ink-receiving layer comprising a synthetic clay. Preferably said synthetic clay is a synthetic layered sodium lithium magnesium silicate.

**EP 0 732 218 A1**

## Description

This invention relates to ink-jet recording elements that contain a polymeric substrate on which are coated ink-receiving layers that can be imaged by the application of liquid ink dots (e.g. by ink-jet printers).

### 2. Background of the invention

Polymeric substrates are becoming more important in the manufacture of ink-jet recording elements for ink-jet printing (e.g. resin coated paper, polyesterfilm, etc). One of the applications of ink-jet recording elements on a polymeric substrate for ink-jet printing is the production of transparencies. These elements are primarily intended for use on an overhead projector. More generally, these elements can be used for all kinds of viewing means by transmitted light. Another application for ink-jet recording elements on a polymeric substrate for ink jet printing involves opaque media intended for direct viewing by the eye, operating according to the principles of reflected light. Such polymeric image recording elements can easily be created by applying liquid ink dots to the ink-receiving layer using equipment such as ink jet printers.

In the ink jet printing technique the individual ink droplets can be applied to the receiving substrate in several different ways. The ink solution can be jetted continuously through a small nozzle towards the receiving layer, said droplets only being selected for areas where a certain image density is required (Hertz method). By combining different droplets into a single pixel cell gray scale printing can be provided by this method of continuous ink jet printing. However, the ink droplet can also be created "upon demand" by a piezoelectric transducer or a thermal push (Bubble Jet), these latter processes being much cheaper than the continuous one and especially suited for low end applications on transparent and opaque polymeric media.

It is known that the ink-receiving layers in ink-jet recording elements must meet different stringent requirements :

- The ink-receiving layer should have a high ink absorbing capacity, so that the dots will not flow out and will not be expanded more than is necessary to obtain a high optical density, even if ink droplet in a multi-color system may be superposed on the same physical spot. ink droplet in a multi-color system may be superposed on the same physical spot.
- The ink-receiving layer should have a high ink absorbing speed (short ink drying time) so that the ink droplets will not feather if smeared immediately after applying.
- The ink receiving layer should be excellent in color forming characteristics.
- The ink dots that are applied to the ink-receiving layer should be smooth at their peripheries and have a shape of a true sphere. The dot diameter must be constant and accurately controlled.
- The receiving layer must be readily wetted so that there is no "puddling", i.e. coalescence of adjacent ink dots, and an earlier absorbed ink drop should not show any "bleeding", i.e. overlap with neighbouring or later placed dots.
- Transparent ink-jet recording elements must, moreover, have a low haze-value and be excellent in transmittance properties.
- After being printed the image must have a good resistance regarding waterfastness, lightfastness and indoor-discoloration.
- The ink-jet recording element may not show any curl or sticky behaviour if stacked before or after being printed.

To meet these requirements, the ink receiving layers of the prior art have been prepared for a long time using many different materials. A dimensionally stable substrate such as polyethyleneterephthalate (PET), cellulosetriacetate, or paper is used most frequently and coated with one or more polymer coatings. These receiving polymer coatings comprise one or more binders and different additives which are helpful to meet the requirements mentioned above.

In the German Patent Application DE 2,234,823 an ink receiving layer comprising gelatin and different particulates and colour molecules is described. US P 3,889,270 describes an image receiving layer comprising a molecular or colloidal disperse phase that enables the jetting ink to penetrate a few microns into this layer. The binder (gelatin, albumin, casein, proteins, polysaccharide, cellulose and its derivatives, (copolymers of) polyvinylalcohol is combined with hydrophylic silica and a white toner.

US P 4,503,111 describes an image receiving layer where a first binder (gelatin or polyvinylalcohol (PVA)) is mixed with a polyvinylpyrrolidone (PVP) having a molecular weight of at least 90000, and for which the ratio PVA/PVP is in the range 3:1 to 1:3. This mixture of PVA, PVP or copolymers can also be combined with a coalesced latex of co-PVA-Polyvinyl-benzylammoniumchloride (US P 4,547,405) yielding a further improvement in waterfastness.

An additional improvement in maximum density and drying time can be obtained using particulates in the binder. Many patent applications have described this effect for many different binder-systems. US P 3,357,846 describes pigments such as kaolin, talc, bariet, TiO<sub>2</sub> used in starch and PVA. US P 3,889,270 describes silica in gelatin, PVA and cellulose. Pigments and particles have also been described in patent applications DE 2,925,769, GB 2,050,866, US P 4,474,850, US P 4,547,405, US 4,578,285, WO 88 06532, US P 4,849,286, EP 339 604, EP 400 681, EP 407 881, EP

411 638 and US 5,045,864.

In US P 4,425,405 a paper support is coated with a layer comprising PVP or a copolymer of vinylacetate and vinylpyrrolidone and a white filler, said filler being selected from the group consisting of calciumcarbonate, clay, talc, calcium-sulfate, diatomaceous earth, aluminiumhydroxide, titaniumdioxide, silica, aluminiumsilicate, satin white, zinc-oxide, and the ratio of said filler versus said binder being in the range 10:1 to 0.2:1.

In US P 4,758,461 a paper for ink jet printing is described in which the outer layer comprises a silicon containing type pigment, said pigment being a synthetic silica (Syloid 620), and said paper showing minimum powder drop-off.

In EP 450,540 an ink jet receiving member is described comprising a substrate, a first pigmented layer and a second pigmented layer, said first pigmented layer comprising aluminiumoxide, said second pigmented layer comprising an aluminiumoxide with lower specific area as said aluminiumoxide used in said first pigmented layer. In an other embodiment said second pigmented layer comprises magnesiumsilicate. In the examples comprising as pigment particles basic magnesiumcarbonate,  $\gamma$ -alumina or alumina, less indoor discoloration is found if compared with the use of synthetic silica as pigment particle.

In EP 461,558 both basic magnesiumcarbonate and a magnesium salt of silicic acid are used in an ink jet receiving member showing improvement in haze, feathering and indoor discoloration.

In many patent applications the tuning of the surface energy and polarity of the receiving layer is done by the use of special (fluoro) tensides: e.g. US P 4,578,285, US P 4,781,985 and US P 5,045,864.

The drying time characteristic can also be improved by a better tuning of the pH value of the coating solution, as described in EP 594896.

An improvement in waterfastness is mostly realised by the use of ammonium mordanting polymers. These polymers interact with most typical ink jet inks resulting in a better localisation of the dye in the binder. Typical examples of such descriptions are US P 4,371,582, US P 4,575,465, US P 4,649,064, GB 2,210,071 and EP 423 829. For instance in US P 4,371,582 a basic polymer latex comprising tertamino- or quaternary ammonium groups is described. In US P 4,575,465 an ink-receiving layer comprising a hydrophilic polymer with up to 50% by weight of vinylpyridine/vinylbenzylquaternary ammonium salt copolymers is claimed. In US P 4,649,064 the quaternary ammonium derivatives are used in combination with calciumacetate, a binder, a suitable crosslinker for the binder, and an ink composition comprising a binder and a crosslinkable dye. In EP-A 609930 polymeric mordanting compounds comprising a phosphonium moiety have been described for use in ink jet receiving layers.

Unfortunately, these transparent ink-jet recording elements with ink-receiving layers that have been described in the prior art fail to combine the criteria mentioned above, especially the combination of improved waterfastness and improved lightfastness at a low fabrication cost.

### 3. Object and summary of the invention:

It is an object of the invention to provide an ink-receiving element that comprises a polymeric film or a resin coated paper as a support and an ink-receiving layer coated thereon in which the element is adapted for use in a printing process where liquid ink dots are applied to it with a high resolution, where the element can be printed by a conventional ink jet ink, resulting in a printed image with both an improved waterfastness and lightfastness.

It is a further object of the present invention to provide an ink-jet recording element for use in ink jet printing that combines an improved waterfastness and lightfastness with a simple and cheap process design.

According to this invention the above objects are realized by providing an ink-jet recording element comprising a polymeric film substrate or a resin coated paper substrate and an ink-receiving layer coated thereon characterized in that said ink-receiving layer comprises a synthetic clay.

### 4. Detailed description of the invention

The present invention is based upon the discovery that some kinds of synthetic clays have an advantageous effect regarding lightfastness and waterfastness if used as single binder or as an additive to the binder(s) in an ink-jet recording element used for the ink-jet printing technique.

Natural clays are essentially hydrous aluminum silicates, wherein alkali metals or alkaline-earth metals are present as principal constituents. Also in some clay minerals magnesium or iron or both replace the aluminum wholly or in part. The ultimate chemical constituents of the clay minerals vary not only in amounts, but also in the way in which they are combined or are present in various clay minerals.

From the natural clays, smectite clays, hectorites and bentonites are well-known. For the said smectite clays some substitutions in both octahedral and tetrahedral layers of the crystal lattice occur, resulting in a small number of inter-layer cations. Smectite clays form a group of "swelling" clays which take up water and organic liquids between the composite layers and which have marked cation exchange capacities.

It is also possible to prepare synthetic clays in the laboratory the properties of which are more reproducible and can be tailor made. According to the present invention synthetic clays are the preferred clays for use as single binder or as

an additive to the binder(s) in an ink-jet recording element used for the ink-jet printing technique. Especially synthetic layered silicates are preferred to be used in ink-receiving layers according to the present invention.

Preferred examples of said synthetic clays, to be used in an ink-receiving layer according to the present invention, include sodium lithium magnesium silicates and sodium lithium magnesium fluoride silicates. It is preferred to use said silicates in the form of a synthetic smectite type clay. Synthetic clays, to be used in ink-receiving layers according to the present invention can be modified with tetrasodium pyrophosphate.

Ink-receiving layers according to the present invention can comprise synthetic clays as sole binder material.

In a preferred embodiment of the present invention the ink-receiving layers in the novel ink-jet recording elements contain said synthetic clay(s) combined with at least one compatible binder which may be selected from the group consisting of:

(1) hydroxyethyl cellulose; (2) hydroxypropyl cellulose; (3) hydroxyethylmethyl cellulose; (4) hydroxypropyl methyl cellulose; (5) hydroxybutylmethyl cellulose; (6) methyl cellulose; (7) sodium carboxymethyl cellulose; (8) sodium carboxymethylhydroxyethyl cellulose; (9) water soluble ethylhydroxyethyl cellulose; (10) cellulose sulfate; (11) polyvinyl alcohol; (12) polyvinyl acetate; (13) polyvinylacetal; (14) polyvinyl pyrrolidone; (15) polyacrylamide; (16) acrylamide/acrylic acid copolymer; (17) styrene/acrylic acid copolymer; (18) ethylene-vinylacetate copolymer; (19) vinylmethyl ether/maleic acid copolymer; (20) poly(2-acrylamido-2-methyl propane sulfonic acid); (21) poly(diethylene triamine-co-adipic acid); (22) polyvinyl pyridine; (23) polyvinyl imidazole; (24) polyimidazoline quaternized; (25) polyethylene imine epichlorohydrinmodified; (26) polyethylene imine ethoxylated; (27) poly(N,N-dimethyl-3,5-dimethylene piperidinium chloride); (28) polyethylene oxide; (29) polyurethane; (30) melamin resins; (31) epoxy resins; (32) urea resins; (33) styrene-butadiene rubbers; (34) chloroprene rubbers; (35) nitrile rubbers; (36) gelatin; (37) carrageenan; (38) dextran; (39) gum arabic; (40) casein; (41) pectin; (42) albumin; (43) starch; (44) collagen derivatives; (45) collodion and (46) agar-agar.

The binder used in combination with synthetic clays in ink receiving layers according to the present invention may also be :

- i. binary blends comprising from about 10 to about 90 percent by weight of polyethylene oxide or gelatine and from about 90 to about 10 percent by weight of an other component selected from the group mentioned above.
- ii. ternary blends comprising from about 10 to about 50 per cent by weight of polyethylene oxide from about 85 to about 5 percent by weight of sodium carboxymethyl cellulose and from about 5 to about 45 percent by weight of an other component selected from the group mentioned above.
- iii. ternary blends comprising from about 10 to about 50 percent by weight of gelatin, from about 85 to about 5 percent by weight of sodium carboxymethyl cellulose and from about 5 to about 45 percent by weight of a component selected from the group mentioned above.
- iv. ternary blends comprised of from about 10 to about 50 percent by weight of gelatin, from about 85 to about 5 percent by weight of polyvinyl pyrrolidone and from about 5 to about 45 percent by weight of an other component selected from the group mentioned above.

Preferred binary blends of binders for use in combination with synthetic clays in ink-receiving layers according to this invention are :

- hydroxyethylmethyl cellulose, 75 percent by weight, and polyethylene oxide, 25 percent by weight;
- gelatin, 80 percent by weight and polyethylene oxide, 20 percent by weight;
- gelatin, 70 percent by weight, and polyvinyl pyrrolidone, 30 percent by weight;
- gelatin, 80 percent by weight, and polyvinylalcohol, 20 percent by weight;
- sodium carboxymethyl cellulose, 80 percent by weight, and gelatin, 20 percent by weight.

Preferred ternary blends of binder materials use in combination with synthetic clays in ink receiving layers according to this invention are :

- gelatin, 50 percent by weight, sodium carboxymethyl cellulose, 25 percent by weight, and polyethylene oxide, 25 percent by weight;
- gelatin, 60 percent by weight, polyvinyl pyrrolidone, 20 percent by weight, and polyvinyl alcohol, 20 percent by weight;
- gelatin, 50 percent by weight, polyvinyl pyrrolidone, 25 percent by weight, and sodium carboxymethyl cellulose, 25 percent by weight.

Preferred binders are gelatin, vinylpyrrolidone and polyvinylalcohol or binary or ternary blends of these. Gelatin is thus a particularly preferred material for use in forming the ink-receiving layer of materials according to this invention.

Among the reasons is the fact that it forms a clear coating, is readily cross-linked in an easily controllable manner, and is highly absorptive of water-based liquid inks to thereby provide rapid-drying characteristics.

When the synthetic clays are blended with other binders as described above, it is preferred that said synthetic clays are present in an amount between 10 and 80 % by weight with respect to the total weight of the binder(s) used in ink-receiving layers according to the present invention. Within said range it is most preferred to use synthetic clays in an amount of 15 to 35 % by weight or in an amount of 50 to 70 % by weight.

The ink-receiving layer according to this invention is preferably cross-linked to provide such desired features as waterfastness and non-blocking characteristics. The cross-linking is also useful in providing abrasion resistance and resistance to the formation of fingerprints on the element as a result of handling. There are a vast number of known cross-linking agents - also known as hardening agents - that will function to cross-link film forming materials, and they are commonly used in the photographic industry to harden gelatin emulsion layers and other layers of photographic silver-halide elements.

Hardening agents can be used individually or in combination and in free or in blocked form. A great many hardeners, useful for the present invention, are known, including formaldehyde and free dialdehydes, such as succinaldehyde and glutaraldehyde, blocked dialdehydes, active esters, sulfonate esters, active halogen compounds, s-triazines and diazines, epoxides, active olefins having two or more active bonds, active olefins, carbodiimides, isoxazolium salts unsubstituted in the 3-position, esters of 2-alkoxy-N-carboxy-dihydroquinoline, N-carbamoyl and N-carbamoylpyridinium salts, hardeners of mixed function, such as halogen-substituted aldehyde acids (e.g. mucochloric and mucobromic acids), onium substituted acroleins and vinyl sulfones and polymeric hardeners, such as dialdehyde starches and copoly(acroleinmethacrylic acid).

The ink-receiving layer in the novel image-recording elements according to this invention may also comprise other particulate material, which may consist either of primary particles comprising single particles or of porous particles comprising secondary particles formed from aggregation of the primary particles. Among these particulate materials, particularly preferable are porous particles having an average particle size of 1-30  $\mu\text{m}$ , preferably 3-10  $\mu\text{m}$  which can be formed by aggregation of smaller particles, having a size of 0.01 to 2  $\mu\text{m}$ , preferably 0.1 to 0.5  $\mu\text{m}$ . These porous particles formed by secondary or tertiary aggregation will not easily disintegrate. The porous material is preferably made of at least one of the organic materials such as polystyrene, polymethacrylate, polymethylmethacrylate, elastomers, ethylene-vinyl acetate copolymers, polyesters, polyester-copolymers, polyacrylates polyvinylethers, polyamides, polyolefines, polysilicones, guanamine resins, polytetrafluoroethylenes, elastomeric styrene-butadiene rubber (SBR), elastomeric butadiene-acrylonitrile rubber (NBR), urea resins, urea-formalin resins, etc., or inorganic materials such as talc, kaolin, diatomaceous earth, calcium carbonate, magnesium carbonate, aluminium hydroxide, aluminium oxide, titanium oxide, zinc oxide, barium sulfate, calcium sulfate, zinc sulfide, satin white, etc. The specific surface area of the particulate material may vary from 10 to 200  $\text{m}^2/\text{g}$  (BET specific surface), and the oil absorption index may range from  $5 \cdot 10^{-6}$  to  $3.5 \cdot 10^{-5} \text{ ms}^{-1/2}$ .

Polymethylmethacrylate beads may be added as matting agents. They are usually added to the receiving layer in a range of 0.4 to 1.2  $\text{g}/\text{m}^2$  and preferably in a range of 0.40 to 0.90  $\text{g}/\text{m}^2$  with 0.50  $\text{g}/\text{m}^2$  being most preferred.

When the element is intended for viewing in reflection, the ink-receiving layer of the invention may contain a whitening agent.  $\text{TiO}_2$  (rutile or anatase) is preferably used as whitening agent in an amount sufficient to produce in the film element a transmission density to white light of at least 0.05, and preferably 0.3 or higher. Amounts of whitener present in the film element can range from 0.1 to 3.0  $\text{g}/\text{m}^2$ , and preferably from 0.2 to 1.5  $\text{g}/\text{m}^2$ , and most preferably 0.7  $\text{g}/\text{m}^2$ . A slurry of the whitener may be added by batchwise addition or by in-line injection just prior to coating the receptor layer(s) on the support.

The ink-receiving layer of the present invention can also comprise a plasticizer such as ethylene glycol, diethylene glycol, propylene glycol, polyethylene glycol, glycerol monomethylether, glycerol monochlorohydrin, ethylene carbonate, propylene carbonate, tetrachlorophthalic anhydride, tetrabromophthalic anhydride urea phosphate, triphenylphosphate, glycerolmonostearate propylene glycol monostearate, tetramethylene sulfone, n-methyl-2-pyrrolidone, n-vinyl-2-pyrrolidone, and polymer latices with low Tg-value such as polyethylacrylate, polymethylacrylate, etc.

Surfactants may be incorporated in the ink-receiving layer of the present invention. They can be any of the cationic, anionic, amphoteric, and nonionic ones as described in JP-62-280068 (1987). Examples of the surfactants are soap, N-alkylamino acid salts, alkylether carboxylic acid salts, acylated peptides, alkylsulfonic acid salts, alkylbenzene and alkyl naphthalene sulfonic acid salts, sulfosuccinic acid salts,  $\alpha$ -olefin sulfonic acid salts, N-acylsulfonic acid salts, sulfonated oils, alkylsulfonic acid salts, alkylether sulfonic acid salts, alkylallylethersulfonic acid salts, alkylamidesulfonic acid salts, alkylphosphoric acid salts, alkyletherphosphoric acid salts, alkylallyletherphosphoric acid salts, alkyl and alkylallylpolyoxyethylene ethers, alkylallylformaldehyde condensed acid salts, alkylallylethersulfonic acid salts, alkylamidesulfonic acid salts, alkylphosphoric acid salts, alkyletherphosphoric acid salts, alkylallyletherphosphoric acid salts, alkyl and alkylallylpolyoxyethylene ethers, alkylallylformaldehyde condensed polyoxyethylene ethers, blocked polymers having polyoxypropylene, polyoxyethylene polyoxypropylalkylethers, polyoxyethyleneether of glycolesters, polyoxyethyleneether of sorbitanesters, polyoxyethyleneether of sorbitolesters, polyethyleneglycol aliphatic acid esters, glycerol esters, sorbitane esters, propyleneglycol esters, sugaresters, fluoro C2-C10 alkylcarboxylic acids, disodium N-per-

fluorooctanesulfonyl glutamate, sodium 3-(fluoro-C6-C11alkyloxy)-1-C3-C4 alkyl sulfonates, sodium 3-( $\omega$ -fluoro-C6-C8 alkanoyl-N-ethylamino)-1-propane sulfonates, N-[3-(perfluorooctanesulfonamide)-propyl]-N,N-dimethyl-N-carboxymethylene ammonium betaine, fluoro-C11-C20 alkylcarboxylic acids, perfluoro C7-C13 alkyl carboxylic acids, perfluorooctane sulfonic acid diethanolamide, Li K and Na perfluoro C4-C12 alkyl sulfonates, N-propyl-N-(2-hydroxyethyl)perfluorooctane sulfonamide, perfluoro C6-C10 alkylsulfonamide propyl sulfonyl glycinate, bis-(N-perfluorooctylsulfonyl-N-ethanolaminoethyl)phosphonate, mono-perfluoro C6-C16 alkyl-ethyl phosphonates, and perfluoroalkylbetaine.

Especially useful are the fluorocarbon surfactants as described in e.g. US P 4,781,985, having a structure of :

$F(CF_2)_{4-9}CH_2CH_2SCH_2CH_2N^+R_3X^-$  wherein R is an hydrogen or an alkyl-group; and in US P 5,084,340, having a structure of:  $CF_3(CF_2)_mCH_2CH_2O(CH_2CH_2O)_nR$  wherein  $m = 2$  to  $10$ ;  $n = 1$  to  $18$ ; R is hydrogen or an alkyl group of 1 to 10 carbon atoms. These surfactants are commercially available from DuPont and 3M. The concentration of the surfactant component in the ink-receiving layer is typically in the range of 0.1 to 2 percent, preferably in the range of 0.4 to 1.5 percent and is most preferably 0.75 percent by weight based on the total dry weight of the layer.

Ink-receiving layers according to the present invention may also comprises mordanting agents. Said mordanting agents can be quarternary ammonium mordanting agent as disclosed in, e.g., US P 4,371,582, US P 4,575,465, US P 4,649,064, GB 2,210,071 and EP 423 829. Said mordanting agent can also be phosphonium mordanting agents as disclosed in, e.g., EP-A 609 930.

The ink-receiving layers of the present invention may additionally comprise different additives which are well known in the art, and include UV-filters and antistatic agents.

The ink-jet recording elements of this invention comprise a polymeric support for the ink-receiving layer. A wide variety of such supports are known and are commonly employed in the art. They include, for example, transparent supports as those used in the manufacture of photographic films including cellulose acetate propionate or cellulose acetate butyrate, polyesters such as poly(ethyleneterephthalate) and poly(ethylenenaphthalate), polyamides, polycarbonates, polyimides, polyolefins, poly(vinylacetals), polyethers and polysulfonamides. Other examples of useful high-quality polymeric supports for the present invention include opaque white polyesters and extrusion blends of poly(ethyleneterephthalate) and polypropylene. Polyester film supports and especially poly(ethyleneterephthalate) are preferred because of their excellent properties of dimensional stability. When such a polyester is used as the support material, a subbing layer must be employed to improve the bonding of the ink-receiving layer to the support. Useful subbing layers for this purpose are well known in the photographic art and include, for example, polymers of vinylidene chloride such as vinylidene chloride/acrylonitrile/acrylic acid terpolymers or vinylidene chloride/methyl acrylate/itaconic acid terpolymers.

The ink-jet recording elements of this invention are employed in printing processes where liquid ink dots are applied to the ink-receiving layer of the element. The method comprises the steps of :

- (i) forming droplets of a pigmented and/or dyed liquid and
- (ii) applying said droplets to an ink-jet recording element according to the present invention.

A typical process is a ink-jet printing process which involves a method of forming the image on a paper or transparency by ejecting ink (i.e. a pigmented and/or dyed liquid) droplets from a print head from one or more nozzles. The ink has not to be liquid at room temperature, but can become liquid upon heating. When ink is described herein as a pigmented and/or dyed liquid it is understood that it has only to be liquid when the droplets are formed. Several schemes can be used to control the deposition of the ink droplets on the image-recording element to form the desired ink dot pattern used to build the image. For example, one method comprises deflecting electrically charged ink droplets by electrostatic means. Another method comprises the ejection of single droplets "upon demand" under the control of a piezoelectric device which can operate by volume change or "wall" motion, or under the control of a thermal excitation.

The inks preferably used to image the image-recording elements of this invention are typically liquid compositions comprising a solvent or carrier liquid, dyes or pigments, humectants, organic solvents, detergents, thickeners, preservatives, etc. The solvent or carrier liquid is predominantly water, although ink in which organic materials such as polyhydric alcohols are used as carrier liquid, can also be used. The dyes used in such ink-jet ink compositions are typically water-soluble direct dyes or acid type dyes.

Such liquid ink compositions have been extensively described in the prior art (US P 4,381,946, US P 4,781,758, US P 4,994,110).

The following examples are presented to illustrate this invention, but not to limit the present invention thereto.

#### EXAMPLE 1

A polyethylene terephthalate film (PET-100  $\mu$ m thick with typical photographic subbing layers, used for a better bonding between the PET and the gelatinous layers) was used as the substrate. The composition A was applied to this

substrate with a pilot coating machine, so as to give a dry film-coating thickness of 5  $\mu\text{m}$ ; chilled at 5°C for 20 s; and dried at 35°C for 120 s (RH=30%).

#### Coating solution A

40 parts of a gelatin with a gel strength higher than 220 g, the viscosity of a 10% solution of it at 40° C being higher than 50 mPas and containing 25 to 30 % microgels were mixed with 10.5 parts of LAPONITE JS, tradename for a synthetic layered sodium lithium magnesium fluoride silicate and commercially available through the Laporte Company, UK, with 10 parts of polymethylmethacrylate polymeric beads with a mean particle diameter of 6.2 micron, with 0.5 parts of a fluorosurfactant, with formula  $\text{C}_7\text{F}_{15}\text{COONH}_4$  (FC126, a commercial product of MMM, Minesota, USA), and with 0.2 parts of formaldehyde. Water was added to give 1170 parts. The pH of the coating solution was adjusted to pH 7 by the addition of citric acid.

#### COMPARATIVE EXAMPLE 1

A recording medium with an ink-receiving transparent layer was prepared as described in example 1, except for the fact that no synthetic clay was added to the coating solution.

#### EXAMPLE 2

A recording medium with an ink-receiving transparent layer was prepared as described in example 1, except for the fact that in stead of 10.5 parts LAPONITE JS, 10 parts of LAPONITE RDS, tradename for a synthetic layered sodium lithium magnesium silicate and commercially available through the Laporte Company UK was used.

#### COMPARATIVE EXAMPLE 2

A recording medium with an ink-receiving transparent layer was prepared as described in example 1, except for the fact that no synthetic clay was added to the coating solution, but as particulate material 20 parts of Silicagel (KIESEL-SOL 300F, a tradename of Bayer AG, Leverkusen Germany for a dispersion of  $\text{SiO}_2$  with a specific surface of 280 to 300  $\text{m}^2/\text{g}$ ) were used.

#### EXAMPLE 3

A recording medium with an ink-receiving layer was prepared as described in example 1, except for the fact that 15 parts of LAPONITE RDS, tradename for a synthetic layered sodium lithium magnesium silicate and commercially available through the Laporte Company UK was used, and that as substrate material a polypropylene-voided polyester as described in EP-A 582 750 was used.

#### COMPARATIVE EXAMPLE 3

A recording medium with an ink-receiving layer was prepared as described in comparative example 1 was prepared, except for the fact that as substrate material a polypropylene-voided polyester as described in example 3 was used.

Before using the recording media from examples 1 to 3 and of comparative examples 1 to 3, the recording media were first acclimatised for at least 2 hours at 25°C and 30%RH, and then a test image was jetted upon it. For the ink application, a Hewlett-Packard DeskJet 500C was used.

The prints on the recording media prepared in this way were evaluated as follows:

1. The optical density (OD) of the three primary colors and black was measured by means of a Macbeth TR-1224 optical densitometer. All measurements for the transparent material were done in transparent mode, all measurements for the opaque material were done in reflection mode.

2. The waterfastness was tested by first measuring the optical density of a printed sample with different primary colors and black; putting the sample in distilled water of 25°C for 2, 5, 10 and 30 s; and after drying in the atmosphere measuring the optical density of the treated sample again. The slope of the plot optical density versus log (time in sec) is inversely related to the waterfastness. In table 1 the values for waterfastness are the average of the slopes of the optical density versus log (time in sec) plot for each of the three primary colors and black times 100 (the lower the figure, the better).

3. The lightfastness was tested by first measuring the optical density of a printed sample with different primary colors and black; placing the sample under a Xenon-tube for 16 hours (Xe 1500; Color temperature = 5500-6500K;

180 kLux;  $T < 45^{\circ}\text{C}$ ); and after this treatment measuring the optical density of the sample again. The remaining optical density is related to the lightfastness. In table 1 the values for lightfastness are the remaining densities expressed as a percentage of the original density (the higher the figure, the better).

The results of these evaluations are given in table 1.

TABLE 1

Property	Example n°					
	1	2	C1	C2	3	C3
OD_Y	0.43	0.52	0.60	0.56	0.63	0.82
OD_M	0.37	0.50	0.57	0.52	0.73	1.10
OD_C	0.71	1.04	1.02	1.01	1.36	1.88
OD_B	0.81	0.80	0.81	0.83	1.29	1.42
Waterfastness	290	235	370	332	248	372
Lightfastness	60	63	51	55	60	40

The ink-receiving layers according to the present invention, examples 1 to 3, present better qualities than the ink-receiving layers according to the prior art (comparative examples 1 to 3).

#### Claims

1. An ink-jet recording element comprising a polymeric film substrate or a resin coated paper substrate and an ink-receiving layer coated thereon characterized in that said ink-receiving layer comprises a synthetic clay.
2. An ink-jet recording element according to claim 1, wherein said ink-receiving layer comprises further a binder.
3. An ink-jet recording element according to claims 1 or 2, wherein said synthetic clay is a synthetic layered silicate comprising lithium, magnesium and sodium ions.
4. An ink-jet recording element according to any of claims 1 to 3, wherein said synthetic clay is a smectite type clay modified with tetrasodium pyrophosphate.
5. An ink-jet recording element according to claims 1 or 2, wherein said synthetic clay is a synthetic layered sodium lithium magnesium fluoride silicate.
6. An ink-jet recording element according to claim 5, wherein said synthetic clay is a smectite type clay modified with tetrasodium pyrophosphate.
7. An ink-jet recording element according to any of claims 2 to 6, wherein said binder is a member selected from the group consisting of gelatin, polyvinyl pyrrolidone and polyvinyl alcohol.
8. An ink-jet recording element according to any of claims 2 to 7, wherein said ink-receiving layer comprises between 10 and 80 % by weight of said synthetic clay.
9. An ink-jet recording element according to any of the preceding claims wherein said polymeric substrate is transparent.
10. An ink-jet recording element according to any of the preceding claims wherein said ink-receiving layer comprises a further porous particulate material.
11. An ink-jet recording element according to any of the preceding claims wherein said ink-receiving layer further comprises a plasticizer.



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12. An ink-jet recording element according to any of the preceding claims wherein said ink-receiving layer further comprises a surfactant.
- 5 13. An ink-jet recording element according to any of the preceding claims wherein said ink-receiving layer further comprises a UV-filter or an antistatic agent or a matting agent.
14. An ink-jet recording element according to any of claims 2 to 13, wherein said ink-receiving layer further contains a hardener.
- 10 15. An ink-jet recording element according to any of the preceding claims wherein said ink-receiving layer comprises a polymer containing phosphonium moieties.
16. Method for ink-jet printing comprising the steps of
- 15 (i) forming droplets of a pigmented and/or dyed liquid and  
(ii) applying said droplets to an ink-jet recording element according to any of the preceding claims.

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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 95 20 0629

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL.6)
X	EP-A-0 633 143 (SONY CORPORATION)  * page 4, line 42 - page 6, line 49; examples * ----	1-3, 5, 7-9, 11, 13, 14, 16	B41M5/00
A	DATABASE WPI Section Ch, Week 8323, Derwent Publications Ltd., London, GB; Class A82, AN 83-55169K & JP-A-58 072 495 (JUJO PAPER MFG KK) 30 April 1983 * abstract * ----	1, 2, 16	
D, A	EP-A-0 609 930 (AGFA GEVAERT NV)  * the whole document * -----	1, 2, 7, 9-16	
The present search report has been drawn up for all claims			<b>TECHNICAL FIELDS SEARCHED (Int.CL.6)</b>  B41M
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>2 August 1995</b>	Examiner <b>Bernardo Noriega, F</b>
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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